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Introduction to Coordination Compounds

Key Characteristics

- Transition metals form complexes by coordinate bonds.
- Central metal atom linked to ions or neutral molecules via lone pair donation.
- Examples: Chlorophyll (Mg), Haemoglobin (Fe), Vitamin B₁₂ (Co).

Solved Examples

- **Ex 1:** Identify the central metal in haemoglobin.
Answer: Iron (Fe).

Practice Set

- Q1: What type of bond links the central metal to ligands in coordination compounds?
A. Ionic bond
B. Covalent bond
C. Coordinate bond
D. Metallic bond
- Q2: Which of the following is a coordination compound?
A. NaCl
B. Haemoglobin
C. H₂O
D. CO₂
- Q3: Which metal is central in vitamin B₁₂?
A. Magnesium
B. Iron
C. Cobalt
D. Copper

Answer Key

- Q1: C - Coordinate bonds form by donation of lone pairs from ligands to metal.
- Q2: B - Haemoglobin is a coordination compound with iron as central metal.
- Q3: C - Cobalt is the central metal in vitamin B₁₂.

Memory Aids

- Coordination compounds = Central metal + ligands via coordinate bonds.
- Remember: Chlorophyll (Mg), Haemoglobin (Fe), Vitamin B₁₂ (Co).

Werners Theory of Coordination Compounds

Main Postulates

- Metals show two valencies: primary (ionisable) and secondary (non-ionisable).
- Primary valency = oxidation state, satisfied by negative ions, non-directional.
- Secondary valency = coordination number, satisfied by ligands, directional, defines geometry.
- Coordination entities are inside square brackets; ions outside are counter ions.
- Common geometries: octahedral, tetrahedral, square planar.
- Examples: [Co(NH₃)₆]³⁺ (octahedral), [Ni(CO)₄] (tetrahedral), [PtCl₄]²⁻ (square planar).

Complex compound	Colour	Number of Cl ⁻ ion precipitated per molecule of the complex by Ag ⁺	Formula
CoCl ₃ · 6NH ₃	Yellow	3	[Co(NH ₃) ₆] ³⁺ 3Cl ⁻
CoCl ₃ · 5NH ₃	Purple	2	[Co(NH ₃) ₅ Cl] ²⁺ 2Cl ⁻
CoCl ₃ · 4NH ₃	Green	1	<i>trans</i> -[Co(NH ₃) ₄ Cl ₂] ⁺ Cl ⁻
CoCl ₃ · 4NH ₃	Violet	1	<i>cis</i> -[Co(NH ₃) ₄ Cl ₂] ⁺ Cl ⁻

The last two complexes in table have identical formula but distinct properties. These are actually *cis*- and *trans*-isomers.

Solved Examples

- **Ex 1:** Determine the coordination number of Co in $[\text{CoCl}(\text{NH}_3)_5]^{2+}$.
Answer: 6 (octahedral geometry).

Practice Set

- Q1: What does the primary valency of a metal represent?
A. Coordination number
B. Oxidation state
C. Number of ligands
D. Number of counter ions
- Q2: Which geometry is common for $[\text{Ni}(\text{CO})_4]$ complex?
A. Octahedral
B. Tetrahedral
C. Square planar
D. Linear
- Q3: In Werner's theory, secondary valency corresponds to:
A. Ionisable valency
B. Coordination number
C. Oxidation state
D. Number of counter ions

Answer Key

- Q1: B - Primary valency = oxidation state of metal.
- Q2: B - $[\text{Ni}(\text{CO})_4]$ has tetrahedral geometry.
- Q3: B - Secondary valency = coordination number, non-ionisable.

Memory Aids

- Primary valency = oxidation state (ionisable).
- Secondary valency = coordination number (defines geometry).
- Common shapes: Octahedral (6), Tetrahedral (4), Square planar (4).

Difference Between Double Salt and Complex

Key Differences

- Both formed by combination of stable compounds in fixed ratio.
- Double salts dissociate into ions in solution.
- Examples of double salts: Carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), Mohr's salt ($\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$), Potash alum ($\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$).
- Complexes do not dissociate into ions easily; ligands remain bonded.

Solved Examples

- **Ex 1:** Identify if Mohr's salt is a double salt or complex.
Answer: Double salt (dissociates into ions).

Practice Set

- Q1: Which of the following is a double salt?
A. $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$
B. $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$
C. $[\text{Ni}(\text{CO})_4]$
D. $[\text{PtCl}_4]^{2-}$
- Q2: Double salts in solution:
A. Do not dissociate
B. Dissociate into ions
C. Form coordinate bonds
D. Are covalent compounds
- Q3: Which property distinguishes complexes from double salts?
A. Stoichiometric ratio
B. Dissociation into ions
C. Formation of coordinate bonds
D. Presence of metal

Answer Key

- Q1: B - $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ is a double salt.
- Q2: B - Double salts dissociate into ions in solution.
- Q3: C - Complexes have coordinate bonds; double salts do not.

Memory Aids

- Double salts dissociate; complexes do not.
- Double salts: Mohr's salt, Carnallite, Potash alum.
- Complexes: Coordinate bonds, fixed geometry.

Coordination Entity/Coordination Sphere

Explanation

- Central metal atom/ion and ligands directly attached are enclosed in square brackets.
- Collectively called coordination sphere or coordination entity.
- Coordination sphere is non-ionisable.

Solved Examples

- In $\text{K}_4[\text{Fe}(\text{CN})_6]$, coordination sphere is $[\text{Fe}(\text{CN})_6]^{4-}$.

Practice Set

- Q1: What is enclosed in the coordination sphere?
 - A. Only ligands
 - B. Only metal ion
 - C. Metal ion and ligands
 - D. Counter ions
- Q2: Which of the following is non-ionisable?
 - A. Coordination sphere

- B. Counter ions
- C. Both
- D. None
- Q3: In $K_4[Fe(CN)_6]$, what is the charge on coordination sphere?
 - A. 4+
 - B. 4-
 - C. Neutral
 - D. 2-

Answer Key

- Q1: C - Coordination sphere includes both metal ion and ligands.
- Q2: A - Coordination sphere is non-ionisable.
- Q3: B - Coordination sphere $[Fe(CN)_6]^{4-}$ has 4- charge.

Memory Aids

- Coordination sphere = [Metal + Ligands]
- Non-ionisable part of complex

Counter Ions

Explanation

- Ionisable groups written outside the coordination sphere brackets.
- Balance the charge of coordination entity.

Solved Examples

- In $K_4[Fe(CN)_6]$, counter ion is K^+ .

Practice Set

- Q1: Where are counter ions written in a coordination compound?
 - A. Inside brackets
 - B. Outside brackets
 - C. Both inside and outside
 - D. None
- Q2: What is the role of counter ions?
 - A. Coordinate with metal
 - B. Balance charge
 - C. Donate electrons
 - D. Form coordinate bonds
- Q3: In $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, what are the counter ions?
 - A. NH_3
 - B. Cl^- outside brackets
 - C. Co^{3+}
 - D. Cl inside brackets

Answer Key

- Q1: B - Counter ions are outside the brackets.
- Q2: B - They balance the charge of the complex.
- Q3: B - Cl^- ions outside brackets are counter ions.

Memory Aids

- Counter ions = outside brackets, ionisable
- Balance complex charge

Central Metal Atom/Ion

Explanation

- Metal atom/ion bonded to ligands by coordinate bonds in definite geometry.

- Acts as Lewis acid (electron pair acceptor).
- Examples: Ni^{2+} in $[\text{NiCl}_2(\text{H}_2\text{O})_4]$, Co^{3+} in $[\text{CoCl}(\text{NH}_3)_5]^{2+}$, Fe^{3+} in $[\text{Fe}(\text{CN})_6]^{3-}$.

Solved Examples

- Identify central metal ion in $[\text{Fe}(\text{CN})_6]^{3-}$: Fe^{3+} .

Practice Set

- Q1: What is the role of central metal ion?
 - A. Electron donor
 - B. Lewis acid
 - C. Ligand
 - D. Counter ion
- Q2: Which is central metal ion in $[\text{Co}(\text{NH}_3)_6]^{3+}$?
 - A. NH_3
 - B. Co^{3+}
 - C. Cl^-
 - D. H_2O
- Q3: Central metal ion in $[\text{NiCl}_2(\text{H}_2\text{O})_4]$ is?
 - A. Ni^{2+}
 - B. Cl^-
 - C. H_2O
 - D. NH_3

Answer Key

- Q1: B - Central metal ion acts as Lewis acid.
- Q2: B - Co^{3+} is central metal ion.
- Q3: A - Ni^{2+} is central metal ion.

Memory Aids

- Central metal = Lewis acid
- Coordinates ligands

Ligands

Explanation

- Molecules or ions donating lone pair to central metal via coordinate bond.
- Types based on donor atoms:
 - Unidentate: single donor atom
 - Didentate: two donor atoms
 - Polydentate: several donor atoms
 - Ambidentate: can coordinate through two different atoms

Solved Examples

- Unidentate ligands: Cl^- , H_2O , NH_3
- Didentate ligands: Ethylenediamine ($\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$), Oxalate ($\text{C}_2\text{O}_4^{2-}$)

Practice Set

- Q1: What type of ligand is NH_3 ?
 - A. Unidentate
 - B. Didentate
 - C. Polydentate
 - D. Ambidentate
- Q2: Which ligand binds through two donor atoms?
 - A. Cl^-
 - B. Ethylenediamine
 - C. H_2O

- D. NO_2^-
- Q3: Ambidentate ligand example is?
 - A. NH_3
 - B. NO_2^-
 - C. EDTA^{4-}
 - D. $\text{C}_2\text{O}_4^{2-}$

Answer Key

- Q1: A - NH_3 is unidentate ligand.
- Q2: B - Ethylenediamine is didentate ligand.
- Q3: B - NO_2^- is ambidentate ligand.

Memory Aids

- Unidentate = 1 donor atom
- Didentate = 2 donor atoms
- Ambidentate = 2 possible donor atoms, binds through one

Polydentate Ligand

Explanation

- Ligand binds through several donor atoms to metal ion.
- Example: EDTA^{4-} .

Solved Examples

- EDTA^{4-} binds through multiple donor atoms forming stable complexes.

Practice Set

- Q1: Polydentate ligand binds through how many donor atoms?
 - A. One
 - B. Two
 - C. Several
 - D. None
- Q2: Which is an example of polydentate ligand?
 - A. NH_3
 - B. EDTA^{4-}
 - C. Cl^-
 - D. NO_2^-
- Q3: Polydentate ligands form complexes that are?
 - A. Unstable
 - B. Stable
 - C. Neutral
 - D. Ionised

Answer Key

- Q1: C - Polydentate ligands bind through several donor atoms.
- Q2: B - EDTA^{4-} is polydentate ligand.
- Q3: B - Polydentate ligands form stable complexes.

Memory Aids

- Polydentate = many donor atoms
- EDTA = common polydentate ligand

Chelate Ligand

Explanation

- Didentate or polydentate ligand forming two or more coordinate bonds with metal.

- Forms 5 or 6 membered ring with metal ion.

Solved Examples

- Ethylene diamine forms chelate ring with metal ion.

Practice Set

- Q1: Chelate ligand forms how many coordinate bonds?
 - A. One
 - B. Two or more
 - C. None
 - D. Only one donor atom
- Q2: Chelate ring size is usually?
 - A. 3 or 4 membered
 - B. 5 or 6 membered
 - C. 7 or 8 membered
 - D. 2 membered
- Q3: Which ligand forms chelate complex?
 - A. NH_3
 - B. EDTA^{4-}
 - C. Cl^-
 - D. NO_2^-

Answer Key

- Q1: B - Chelate ligands form two or more coordinate bonds.
- Q2: B - Chelate rings are 5 or 6 membered.
- Q3: B - EDTA^{4-} forms chelate complexes.

Memory Aids

- Chelate = ring formation with metal

- 5 or 6 membered rings are most stable

Ambidentate Ligand

Explanation

- Unidentate ligand that can coordinate through two different atoms.
- Examples: NO_2^- , SCN^- .

Solved Examples

- NO_2^- can bind through N or O atom.

Practice Set

- Q1: Ambidentate ligand binds through?
 - A. One fixed atom
 - B. Two different atoms alternatively
 - C. Several atoms simultaneously
 - D. None
- Q2: Which is an ambidentate ligand?
 - A. NH_3
 - B. NO_2^-
 - C. EDTA^{4-}
 - D. Cl^-
- Q3: SCN^- binds through?
 - A. S atom
 - B. N atom
 - C. Both S or N
 - D. O atom

Answer Key

- Q1: B - Ambidentate ligands can bind through two different atoms alternatively.
- Q2: B - NO_2^- is ambidentate ligand.
- Q3: C - SCN^- can bind through S or N atom.

Memory Aids

- Ambidentate = two possible donor atoms
- Binding site depends on conditions

Coordination Number

Explanation

- Total number of coordinate bonds between central metal and ligands.
- Examples:
 - $[\text{PtCl}_6]^{2-}$ coordination number = 6
 - $[\text{Ni}(\text{NH}_3)_4]^{2+}$ coordination number = 4
 - $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ coordination number = 6 (oxalate is didentate)
 - $[\text{Co}(\text{en})_3]^{3+}$ coordination number = 6 (en = ethane-1,2-diamine, didentate)

Solved Examples

- Find coordination number of Ni in $[\text{Ni}(\text{NH}_3)_4]^{2+}$: 4

Practice Set

- Q1: Coordination number is number of?
 - A. Ligands
 - B. Coordinate bonds

- C. Metal atoms
- D. Counter ions
- Q2: Coordination number of Fe in $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ is?
 - A. 3
 - B. 6
 - C. 4
 - D. 2
- Q3: Coordination number of Pt in $[\text{PtCl}_6]^{2-}$ is?
 - A. 4
 - B. 6
 - C. 2
 - D. 1

Answer Key

- Q1: B - Coordination number counts coordinate bonds.
- Q2: B - Oxalate is didentate, total 6 bonds.
- Q3: B - Pt has 6 coordinate bonds with Cl ligands.

Memory Aids

- Coordination number = total coordinate bonds
- Didentate ligands count twice

Coordination Polyhedron

Explanation

- Spatial arrangement of ligands around central metal ion.
- Determines geometry of complex.

Solved Examples

- Octahedral, tetrahedral, square planar are common coordination polyhedra.

Practice Set

- Q1: Coordination polyhedron describes?
 - A. Ligand types
 - B. Spatial arrangement of ligands
 - C. Metal ion charge
 - D. Counter ions
- Q2: Which geometry is common for coordination number 6?
 - A. Tetrahedral
 - B. Octahedral
 - C. Square planar
 - D. Linear
- Q3: Coordination polyhedron affects?
 - A. Stability
 - B. Color
 - C. Magnetic properties
 - D. All of the above

Answer Key

- Q1: B - It describes spatial arrangement of ligands.
- Q2: B - Octahedral geometry is common for coordination number 6.
- Q3: D - Geometry affects stability, color, magnetism.

Memory Aids

- Octahedral = 6 ligands
- Tetrahedral = 4 ligands
- Square planar = 4 ligands, different geometry

Oxidation Number

Explanation

- Charge on central metal if ligands removed with shared electron pairs.
- Represented by Roman numeral in parentheses after name.
- Example: Cu in $[\text{Cu}(\text{CN})_4]^{3-}$ is +1, written as Cu(I).

Solved Examples

- Oxidation number of Fe in $[\text{Fe}(\text{CN})_6]^{3-}$ is +3.

Practice Set

- Q1: Oxidation number represents?
 - A. Total electrons in complex
 - B. Charge on metal after ligand removal
 - C. Number of ligands
 - D. Number of counter ions
- Q2: Oxidation number of Cu in $[\text{Cu}(\text{CN})_4]^{3-}$ is?
 - A. +1
 - B. +2
 - C. 0
 - D. -1
- Q3: How is oxidation number represented?
 - A. Arabic numeral
 - B. Roman numeral in parentheses
 - C. Chemical symbol
 - D. Charge outside brackets

Answer Key

- Q1: B - Charge on metal after removing ligands.
- Q2: A - Cu is +1 in given complex.

- Q3: B - Roman numeral in parentheses.

Memory Aids

- Oxidation number = metal charge after ligand removal
- Use Roman numerals in names

Homoleptic Complex

Explanation

- Metal ion bound to only one kind of ligand.
- Example: $[\text{Co}(\text{NH}_3)_6]^{3+}$.

Solved Examples

- $[\text{Co}(\text{NH}_3)_6]^{3+}$ is homoleptic complex.

Practice Set

- Q1: Homoleptic complex has how many ligand types?
 - A. One
 - B. Two
 - C. More than two
 - D. None
- Q2: Which is homoleptic?
 - A. $[\text{Co}(\text{NH}_3)_6]^{3+}$
 - B. $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$
 - C. $[\text{Fe}(\text{CN})_6]^{3-}$
 - D. $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$
- Q3: Homoleptic complexes are generally?
 - A. Mixed ligands

- B. Single ligand type
- C. Unstable
- D. Ionised

Answer Key

- Q1: A - Only one ligand type.
- Q2: A - $[\text{Co}(\text{NH}_3)_6]^{3+}$ has only NH_3 ligands.
- Q3: B - Homoleptic means single ligand type.

Memory Aids

- Homo = same ligands
- Single ligand type only

Heteroleptic Complex

Explanation

- Metal ion bound to more than one kind of ligand.
- Example: $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$.

Solved Examples

- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ is heteroleptic complex.

Practice Set

- Q1: Heteroleptic complex has how many ligand types?
 - A. One
 - B. More than one

- C. None
- D. Only metal ion
- Q2: Which is heteroleptic?
 - A. $[\text{Co}(\text{NH}_3)_6]^{3+}$
 - B. $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$
 - C. $[\text{Fe}(\text{CN})_6]^{3-}$
 - D. $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$
- Q3: Heteroleptic complexes are generally?
 - A. Mixed ligands
 - B. Single ligand type
 - C. Unstable
 - D. Ionised

Answer Key

- Q1: B - More than one ligand type.
- Q2: B - $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ has NH_3 and Cl ligands.
- Q3: A - Heteroleptic means mixed ligands.

Memory Aids

- Hetero = different ligands
- More than one ligand type

Effective Atomic Number Rule (EAN Rule)

Explanation

- EAN = Atomic number of metal - electrons lost + electrons gained from ligands.
- Used to predict stability of complexes.
- Examples following EAN: $[\text{Pd}(\text{NH}_3)_6]^{4+}$, $[\text{Pt}(\text{NH}_3)_6]^{4+}$, $[\text{Cu}(\text{CN})_4]^{3-}$.
- Examples not following EAN but stable: $[\text{PdCl}_4]^{2-}$, $[\text{Ag}(\text{NH}_3)_2]^+$, $[\text{Ni}(\text{CN})_4]^{2-}$, $[\text{Ni}(\text{en})_3]^{2+}$.

Solved Examples

- Calculate EAN for $[\text{Cu}(\text{CN})_4]^{3-}$:
 - Cu atomic no. = 29
 - Electrons lost = +1 (Cu(I))
 - Electrons from 4 CN ligands = 8
 - EAN = $29 - 1 + 8 = 36$

Practice Set

- Q1: EAN formula is?
 - A. Atomic no. + electrons lost - electrons from ligands
 - B. Atomic no. - electrons lost + electrons from ligands
 - C. Atomic no. + electrons lost + electrons from ligands
 - D. Atomic no. - electrons lost - electrons from ligands
- Q2: Which complex follows EAN rule?
 - A. $[\text{PdCl}_4]^{2-}$
 - B. $[\text{Pd}(\text{NH}_3)_6]^{4+}$
 - C. $[\text{Ag}(\text{NH}_3)_2]^+$
 - D. $[\text{Ni}(\text{en})_3]^{2+}$
- Q3: EAN of $[\text{Cu}(\text{CN})_4]^{3-}$ is?
 - A. 36
 - B. 34
 - C. 50
 - D. 52

Answer Key

- Q1: B - EAN = Atomic no. - electrons lost + electrons from ligands.
- Q2: B - $[\text{Pd}(\text{NH}_3)_6]^{4+}$ follows EAN.
- Q3: A - EAN calculated as 36.

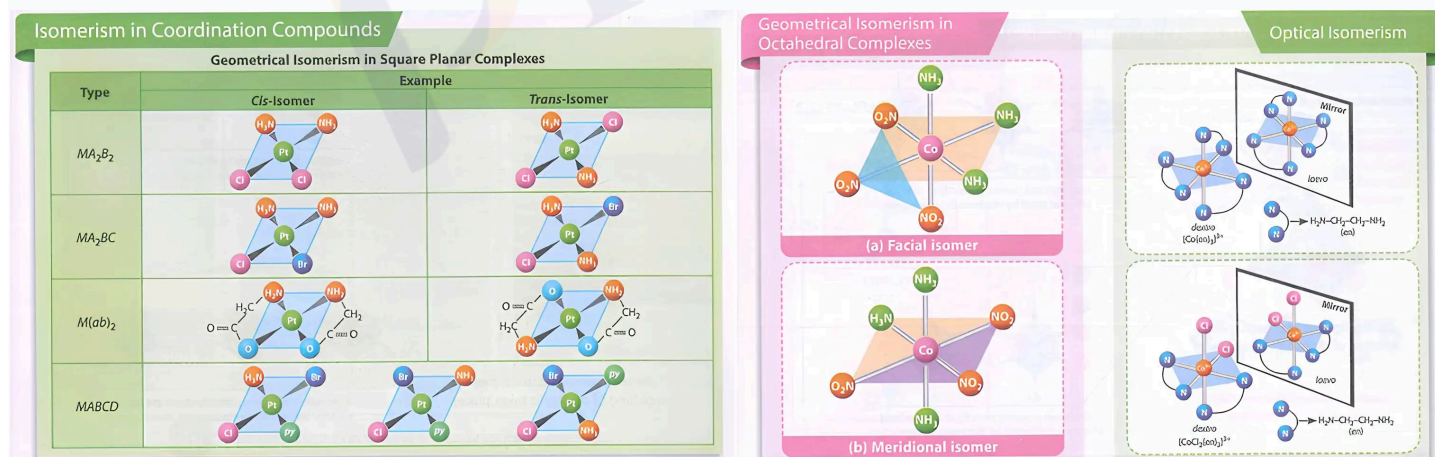
Memory Aids

- EAN = Atomic no. - lost + gained electrons
- Stable complexes often follow EAN

Isomerism in Coordination Compounds

Types of Isomerism

- **Geometrical Isomerism:** Different spatial arrangements of ligands around the metal center.
- **Square Planar Complexes:**
 - **Cis-isomer:** Similar ligands adjacent.
 - **Trans-isomer:** Similar ligands opposite.
- **Octahedral Complexes:**
 - **Facial (fac) isomer:** Three identical ligands on one face.
 - **Meridional (mer) isomer:** Three identical ligands in a plane through the center.
- **Optical Isomerism:** Non-superimposable mirror images (enantiomers) that rotate plane-polarized light differently.



Solved Examples

- **Ex 1:** Identify cis and trans isomers in $[Pt(NH_3)_2Cl_2]$ (square planar).
Step 1: Locate similar ligands.
Step 2: If adjacent, it is cis; if opposite, trans.

- **Ex 2:** Distinguish fac and mer isomers in $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ (octahedral).

Step 1: Check positions of three Cl ligands.

Step 2: If on one face, fac; if in a plane, mer.

Practice Set

- Q1: In a square planar complex, which arrangement corresponds to trans isomer?
A. Similar ligands adjacent
B. Similar ligands opposite
C. All ligands different
D. None of these
- Q2: Which is true for facial (fac) isomer in octahedral complexes?
A. Three identical ligands in a plane
B. Three identical ligands on one face
C. Two ligands opposite
D. Mirror images
- Q3: Optical isomers are:
A. Superimposable mirror images
B. Non-superimposable mirror images
C. Geometrical isomers
D. Ionisation isomers

Answer Key

- Q1: B - Trans isomer has similar ligands opposite each other.
- Q2: B - Fac isomer has three identical ligands on one face of octahedron.
- Q3: B - Optical isomers are non-superimposable mirror images.

Memory Aids

- "Cis" = "Side by side"; "Trans" = "Across"
- Facial = Face of octahedron; Meridional = Meridian plane
- Optical isomers = Like left and right hands

Classification of Isomerism

Structural Isomerism

- Different ligands or ions within coordination spheres.
- **Ionisation Isomerism:** Different ions released in solution.
- **Hydrate/Solvate Isomerism:** Variation in water molecules inside/outside coordination sphere.
- **Linkage Isomerism:** Ligands bind through different atoms (e.g., NO_2^- via N or O).
- **Coordination Isomerism:** Ligand exchange between cationic and anionic complexes.

Stereoisomerism

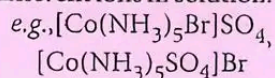
- Same ligands, different spatial arrangement.
- **Geometrical Isomerism:** Cis/trans arrangements in octahedral and square planar complexes.
- **Optical Isomerism:** Non-superimposable mirror images (enantiomers) rotating plane-polarized light differently.

Structural isomerism

Coordination compounds having different ligands within their coordination spheres.

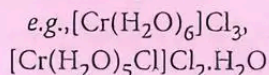
Ionisation isomerism

Complexes that give different ions in solution.



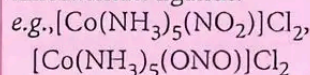
Hydrate/Solvate isomerism

Complexes that differ in number of water molecules present as ligands (inside the coordination sphere) and as free molecules (outside the coordination sphere).



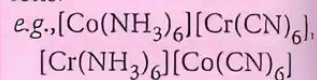
Linkage isomerism

Complexes that differ in the atom of a ligand directly bonded to the metal atom, shown by complexes containing ambidentate ligands.



Coordination isomerism

Occurs when both positive and negative ions are complex ions and two isomers differ in ligand's distribution in two complex ions.



Stereoisomerism

Coordination compounds having different positions and arrangements of ligands in space.

Geometrical isomerism

Arises in heteroleptic complexes due to different possible geometric arrangements of the ligands.

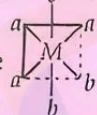
In octahedral complex $[\text{Ma}_3\text{b}_3]$

Facial (fac) : 3 donor atoms of same ligands occupy adjacent positions at the corners.

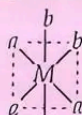


Meridional (mer) :

When the positions are around the meridian.



In octahedral complex $[\text{Ma}_4\text{b}_2]$



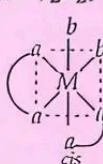
cis



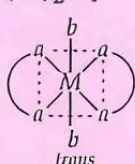
trans

In octahedral complex

$[\text{M}(\text{aa})_2\text{b}_2]$ or $[\text{M}(\text{aa})_2\text{bc}]$



cis



trans

In square planar complex $[\text{Ma}_2\text{b}_2]$

cis : 2 same ligands are arranged adjacent to each other.



trans : 2 same ligands are arranged opposite to each other.



In square planar complex $[\text{Ma}_2\text{bc}]$



cis



trans

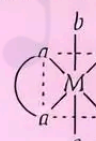
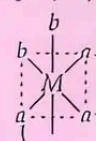
In square planar complex $[\text{Mabcd}]$

These isomers are obtained by selecting 1 ligand, (a) and then placing the remaining 3 ligands (b, c and d), one by one, trans to ligand (a). Shows three isomers – two cis and one trans.

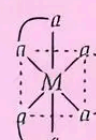
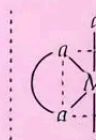
Optical isomerism

Occurs when a complex is represented by two different structures which are non-superimposable mirror images of each other called enantiomers.

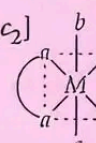
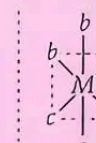
Optical isomerism in $[\text{M}(\text{aa})_2\text{b}_2]$



$[\text{M}(\text{aa})_3]$



$[\text{M}(\text{aa})_2\text{b}_2\text{c}_2]$



dextro (d) : Rotates plane of polarised light to right.

laevo (l) : Rotates plane of polarised light to left.

Solved Examples

- Ex 1:** Identify ionisation isomers in $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$.

Step 1: Check ions released in solution.

Step 2: Different ions indicate ionisation isomers.

- **Ex 2:** Determine linkage isomerism in $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{ClO}_4$.

Step 1: Identify ligand binding atom (N or O).

Step 2: Different binding sites indicate linkage isomers.

Practice Set

- Q1: Which is an example of coordination isomerism?
A. $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$
B. $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$
C. $\text{Cis-}[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$
D. Optical isomers
- Q2: Hydrate isomerism differs in:
A. Number of ligands
B. Number of water molecules
C. Metal center
D. Charge on complex
- Q3: Linkage isomerism occurs due to:
A. Different ligand atoms binding
B. Different ions released
C. Different spatial arrangement
D. Ligand exchange between ions

Answer Key

- Q1: A - Coordination isomerism involves ligand exchange between cation and anion complexes.
- Q2: B - Hydrate isomers differ in water molecules inside/outside coordination sphere.
- Q3: A - Linkage isomerism arises from ligands binding through different atoms.

Memory Aids

- Ionisation = Different ions in solution
- Hydrate = Water molecule variation
- Linkage = Ligand binds via different atoms
- Coordination = Ligand swap between ions

Optical and Geometrical Isomerism Details

Optical Isomerism

- Non-superimposable mirror images called enantiomers.
- Rotate plane-polarized light in opposite directions: Dextro (+) and Laevo (-).
- Optically inactive forms (meso, racemic, dl) do not rotate light due to internal or external compensation.
- Example: Octahedral complex $[\text{Pt}(\text{Py})(\text{NH}_3)(\text{NO}_2)(\text{Cl})(\text{Br})(\text{I})]$ has 15 possible geometrical isomers; each has d and l optical forms, total 30 optically active isomers.

Geometrical Isomerism

- Different spatial arrangements of ligands in octahedral and square planar complexes.
- 15 theoretical geometrical isomers possible for octahedral complex with six different monodentate ligands.
- Only 3 geometrical isomers isolated experimentally for $[\text{Pt}(\text{Py})(\text{NH}_3)(\text{NO}_2)(\text{Cl})(\text{Br})(\text{I})]$.

Solved Examples

- **Ex 1:** Calculate total optically active isomers for $[\text{Pt}(\text{Py})(\text{NH}_3)(\text{NO}_2)(\text{Cl})(\text{Br})(\text{I})]$.
Step 1: 15 geometrical isomers.
Step 2: Each has d and l forms.
Step 3: Total = $15 \times 2 = 30$.

Practice Set

- Q1: Optical isomers are:
 - A. Superimposable mirror images
 - B. Non-superimposable mirror images
 - C. Geometrical isomers
 - D. Ionisation isomers
- Q2: An optically inactive isomer is called:
 - A. Enantiomer

B. Meso form

C. D form

D. L form

- Q3: How many geometrical isomers are theoretically possible for $[\text{Pt}(\text{Py})(\text{NH}_3)(\text{NO}_2)(\text{Cl})(\text{Br})]$ (I)?
 - A. 3
 - B. 6
 - C. 15
 - D. 30

Answer Key

- Q1: B - Optical isomers are non-superimposable mirror images.
- Q2: B - Meso form is optically inactive due to internal compensation.
- Q3: C - 15 geometrical isomers are theoretically possible.

Memory Aids

- Optical isomers = Left and right hands
- Meso = Optically inactive
- Geometrical = Cis/trans arrangements

Bonding in Metal Carbonyls

Overview

- Transition metal carbonyls are organometallic compounds with only CO ligands (homoleptic carbonyls).
- Metal-carbon bond has both sigma (σ) and pi (π) character.
- Bond formation involves sigma donation from CO to metal and pi back-donation from metal to CO (back bonding).
- Back bonding stabilizes the metal-ligand interaction (synergic effect).

Solved Examples

- Ex 1: Describe bonding in $\text{Fe}(\text{CO})_5$.
 - CO donates lone pair to Fe forming σ bond.
 - Fe d-orbitals back-donate electrons to CO π^* orbitals forming π bond.
 - Result: strong Fe-CO bond with synergic effect.

Practice Set

- Q1: What type of bonding is present in metal carbonyls?
 - A) Only σ bonding
 - B) Only π bonding
 - C) Both σ and π bonding
 - D) Ionic bonding
- Q2: Back bonding in metal carbonyls involves overlap of
 - A) Metal d-orbitals with CO lone pair
 - B) Metal d-orbitals with CO π^* orbitals
 - C) CO lone pair with metal s-orbitals
 - D) Metal s-orbitals with CO π orbitals
- Q3: Synergic effect in metal carbonyls refers to
 - A) Strengthening of metal-ligand bond by combined σ and π bonding
 - B) Weakening of metal-ligand bond
 - C) Only σ bonding effect
 - D) Only π bonding effect

Answer Key

- Q1: C - Metal carbonyls have both σ and π bonding.
- Q2: B - Back bonding is metal d-orbitals overlapping with CO π^* orbitals.
- Q3: A - Synergic effect is the combined strengthening by σ and π bonding.

Memory Aids

- Remember: CO donates electrons via σ bond; metal returns electrons via π back bonding.
- Synergic effect = mutual strengthening of bonds.

Examples of Metal Carbonyls

Mononuclear Carbonyls

- $\text{V}(\text{CO})_5$ - Pentacarbonylvanadium (0)
- $\text{Cr}(\text{CO})_6$ - Hexacarbonylchromium (0)
- $\text{Mo}(\text{CO})_6$ - Hexacarbonylmolybdenum (0)
- $\text{W}(\text{CO})_6$ - Hexacarbonyltungsten (0)
- $\text{Ni}(\text{CO})_4$ - Tetracarbonylnickel (0)
- $\text{Fe}(\text{CO})_5$ - Pentacarbonyliron (0)

Polynuclear Carbonyls

- $\text{Co}_2(\text{CO})_8$ - Octacarbonyldicobalt (0)
- $\text{Co}_4(\text{CO})_{12}$ - Dodecacarbonyltetracobalt (0)
- $\text{Mn}_2(\text{CO})_{10}$ - Decacarbonyldimanganese (0)

Solved Examples

- Ex 1: Identify the formula of hexacarbonylchromium.
 - Answer: $\text{Cr}(\text{CO})_6$
- Ex 2: Name $\text{Ni}(\text{CO})_4$.
 - Answer: Tetracarbonylnickel (0)

Practice Set

- Q1: Which is a mononuclear carbonyl?
 - A) $\text{Co}_2(\text{CO})_8$
 - B) $\text{Ni}(\text{CO})_4$
 - C) $\text{Co}_4(\text{CO})_{12}$
 - D) $\text{Mn}_2(\text{CO})_{10}$
- Q2: The formula of pentacarbonyliron is

- A) $\text{Fe}(\text{CO})_4$
- B) $\text{Fe}(\text{CO})_5$
- C) $\text{Fe}(\text{CO})_6$
- D) $\text{Fe}_2(\text{CO})_{10}$
- Q3: Which polynuclear carbonyl has 12 CO ligands?
 - A) $\text{Co}_2(\text{CO})_8$
 - B) $\text{Co}_4(\text{CO})_{12}$
 - C) $\text{Mn}_2(\text{CO})_{10}$
 - D) $\text{Ni}(\text{CO})_4$

Answer Key

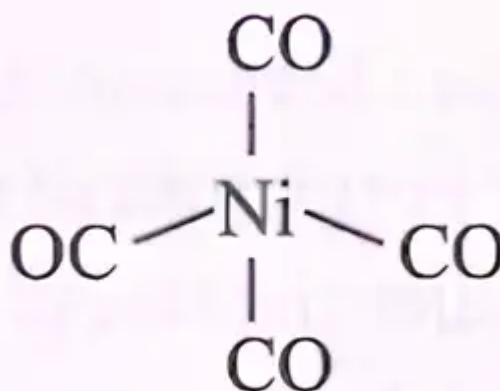
- Q1: B - $\text{Ni}(\text{CO})_4$ is mononuclear.
- Q2: B - Pentacarbonyliron is $\text{Fe}(\text{CO})_5$.
- Q3: B - $\text{Co}_4(\text{CO})_{12}$ has 12 CO ligands.

Memory Aids

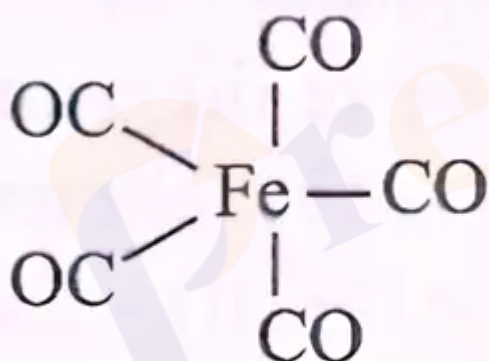
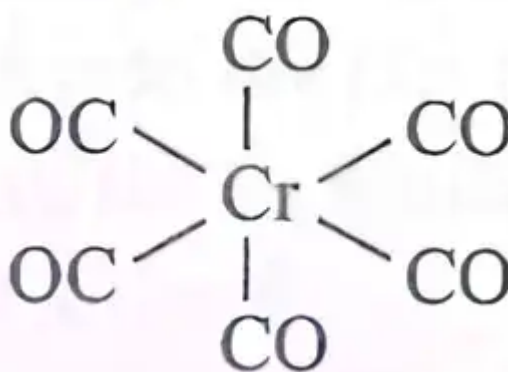
- Mononuclear: $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$, $\text{Cr}(\text{CO})_6$
- Polynuclear: $\text{Co}_2(\text{CO})_8$, $\text{Co}_4(\text{CO})_{12}$, $\text{Mn}_2(\text{CO})_{10}$

Structures of Metal Carbonyls

Common Structures

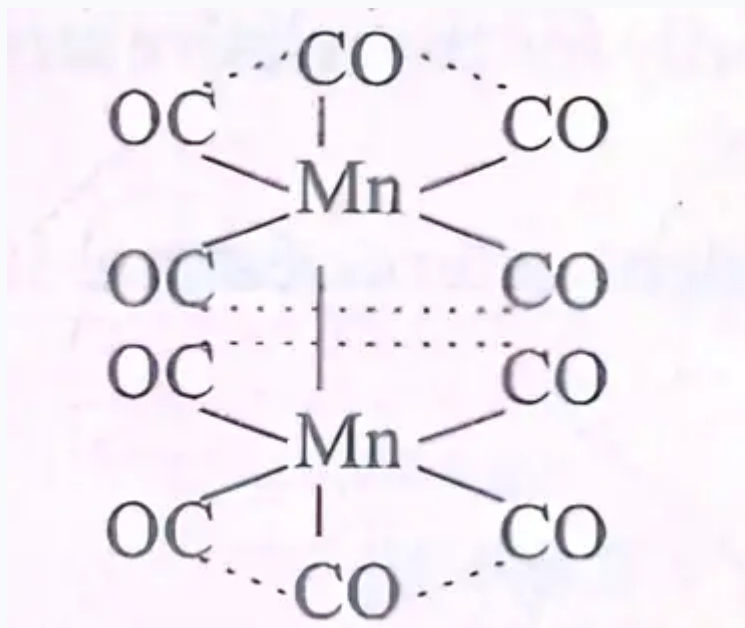


- Ni(CO)_4 : Tetrahedral geometry.
- Fe(CO)_5 : Trigonal bipyramidal geometry.

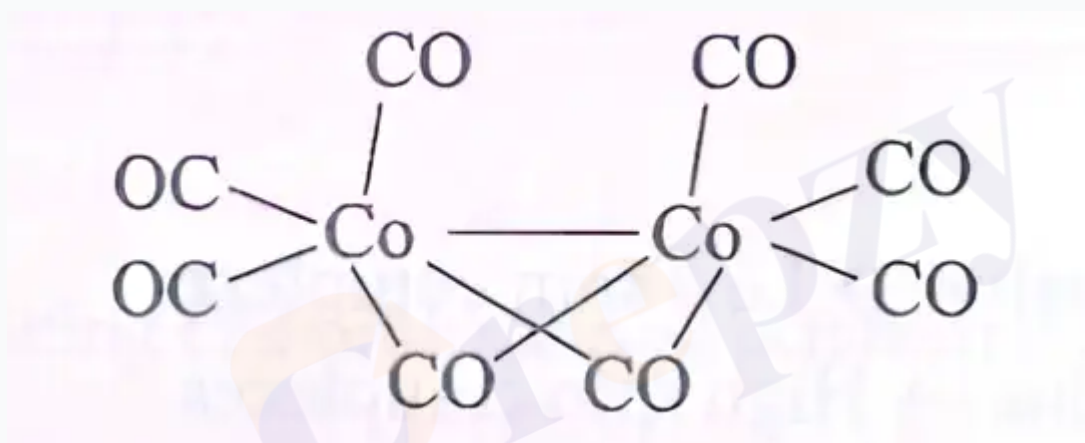


- Cr(CO)_6 : Octahedral geometry.

- $\text{Mn}_2(\text{CO})_{10}$: Two square pyramidal units joined by Mn–Mn bond.



- $\text{Co}_2(\text{CO})_8$: Co–Co bond bridged by two CO ligands.



Solved Examples

- Ex 1: Identify geometry of $\text{Ni}(\text{CO})_4$.
 - Tetrahedral
- Ex 2: Describe bonding in $\text{Mn}_2(\text{CO})_{10}$.
 - Two Mn atoms bonded; each Mn bonded to 5 CO groups.
 - Structure: two square pyramids joined by Mn–Mn bond.

Practice Set

- Q1: Geometry of $\text{Fe}(\text{CO})_5$ is
 - A) Tetrahedral

- B) Square planar
- C) Trigonal bipyramidal
- D) Octahedral
- Q2: $\text{Mn}_2(\text{CO})_{10}$ consists of
 - A) Two octahedrons
 - B) Two square pyramids joined by Mn–Mn bond
 - C) One tetrahedron and one octahedron
 - D) One square planar and one tetrahedron
- Q3: $\text{Co}_2(\text{CO})_8$ has
 - A) Co–Co bond bridged by two CO ligands
 - B) No metal-metal bond
 - C) Single Co atom
 - D) Octahedral geometry

Answer Key

- Q1: C - $\text{Fe}(\text{CO})_5$ is trigonal bipyramidal.
- Q2: B - $\text{Mn}_2(\text{CO})_{10}$ has two square pyramids joined by Mn–Mn bond.
- Q3: A - $\text{Co}_2(\text{CO})_8$ has Co–Co bond bridged by two CO ligands.

Memory Aids

- $\text{Ni}(\text{CO})_4$ - Tetrahedral
- $\text{Fe}(\text{CO})_5$ - Trigonal bipyramidal
- $\text{Cr}(\text{CO})_6$ - Octahedral
- $\text{Mn}_2(\text{CO})_{10}$ - Two square pyramids joined
- $\text{Co}_2(\text{CO})_8$ - Metal-metal bond bridged by CO

Stability of Coordination Compounds

Factors Affecting Stability

- Stability refers to the degree of association in equilibrium: $\text{M} + 4\text{L} \rightleftharpoons \text{ML}_4$
- Magnitude of equilibrium constant (K) expresses stability.

- Factors affecting stability:
 - **Charge on metal ion:** Higher charge increases stability.
 - **Basic nature of ligand:** Stronger base ligands increase stability.
 - **Chelate rings:** Presence increases stability.
 - **Size of metal ion:** Smaller size increases stability.
 - **Electronegativity and polarising power:** Higher values increase stability.

Irving-Williams Order

- Stability order of divalent first-row transition metal ions:
 - $\text{Mn(II)} < \text{Fe(II)} < \text{Co(II)} < \text{Ni(II)} < \text{Cu(II)} > \text{Zn(II)}$

Solved Examples

- Ex 1: Which metal ion forms the most stable complex?
 - Answer: Cu(II) as per Irving-Williams order.

Practice Set

- Q1: Stability of coordination complex increases with
 - A) Decreasing metal ion charge
 - B) Increasing ligand basicity
 - C) Larger metal ion size
 - D) Decreasing polarising power
- Q2: Which factor does NOT increase complex stability?
 - A) Chelate ring formation
 - B) Smaller metal ion size
 - C) Lower metal ion charge
 - D) Higher electronegativity of metal ion
- Q3: According to Irving-Williams order, which ion forms the least stable complex?
 - A) Mn(II)
 - B) Cu(II)
 - C) Ni(II)
 - D) Zn(II)

Answer Key

- Q1: B - Increasing ligand basicity increases stability.
- Q2: C - Lower metal ion charge decreases stability.
- Q3: A - Mn(II) forms the least stable complex.

Memory Aids

- Irving-Williams order mnemonic: "My Fe Co Ni Cu Zn" (increasing stability)
- Chelate rings always increase stability.

Importance and Applications of Coordination Compounds

Qualitative and quantitative analysis

- Dimethyl glyoxime (DMG) forms a coordination compound with Ni(II) used to detect nickel.
- Cobalt is detected using coordination compound with α -nitroso- β -naphthol.
- EDTA acts as a ligand for detection and estimation of many metal ions.
- Water hardness is estimated by titration with Na_2EDTA ; Ca^{2+} and Mg^{2+} form stable complexes with EDTA.
- Selective estimation of Ca^{2+} and Mg^{2+} is possible due to different stability constants.

Extraction of metals

- Many metals are extracted as coordination compounds from ores.
- Silver and gold are extracted as cyanide complexes: $[\text{Ag}(\text{CN})_2]^-$ and $[\text{Au}(\text{CN})_2]^-$.
- Metals can be precipitated from solution by adding zinc.

Purification of metals

- Purification involves formation and decomposition of coordination compounds.

- Example: Impure Ni forms $\text{Ni}(\text{CO})_4$, which decomposes to give pure nickel.

In biological systems

- Chlorophyll: Mg-complex with macrocyclic porphyrin, responsible for photosynthesis.
- Haemoglobin: Fe-complex with macrocyclic porphyrin, carries oxygen in blood.
- Myoglobin: Stores oxygen and regulates respiration.
- Vitamin B-12 (cyanocobalamin): Cobalt complex essential for health.
- Enzymes like carboxypeptidase-A are Zn complexes with proteins.

Catalysts

- Organometallic compounds act as catalysts.
- Ziegler-Natta catalyst $[\text{TiCl}_4(\text{C}_2\text{H}_5)_3\text{Al}]$ polymerizes alkenes at room temperature and pressure.
- Wilkinson's catalyst $[\text{RhCl}(\text{PPh}_3)_3]$ catalyzes hydrogenation.
- Metal carbonyls serve as industrial catalysts.
- Electroplating with silver and gold is smoother from complexes $[\text{Ag}(\text{CN})_2]^-$ and $[\text{Au}(\text{CN})_2]^-$.
- In black and white photography, hypo solution fixes film by forming $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$ complex.

Treatment of diseases

- Medicines often used as coordination compounds.
- Excess toxic metals removed by chelating agents like penicillamine and desferrioxime-B.
- EDTA treats lead poisoning.
- Cis-platin $[\text{PtCl}_2(\text{NH}_3)_2]$ used in cancer treatment.

Solved Examples

- **Ex 1:** Detection of Ni using DMG
 - Mix sample with DMG solution.
 - Formation of red precipitate confirms Ni presence.

- **Ex 2:** Estimation of water hardness
 - Titrate water sample with Na_2EDTA .
 - Calculate Ca^{2+} and Mg^{2+} concentration from volume used.
- **Ex 3:** Purification of Ni
 - Impure Ni reacts with CO to form $\text{Ni}(\text{CO})_4$ gas.
 - Decompose $\text{Ni}(\text{CO})_4$ to get pure Ni metal.

Practice Set

- **Q1:** Which ligand is used to detect Ni(II)?
 - A. α -nitroso- β -naphthol
 - B. Dimethyl glyoxime
 - C. EDTA
 - D. Penicillamine
- **Q2:** Which complex is used in the extraction of gold?
 - A. $[\text{Au}(\text{CN})_2]^-$
 - B. $\text{Ni}(\text{CO})_4$
 - C. $[\text{RhCl}(\text{PPh}_3)_3]$
 - D. $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$
- **Q3:** Which coordination compound is used in cancer treatment?
 - A. EDTA
 - B. Cis-platin
 - C. Vitamin B-12
 - D. Ziegler-Natta catalyst

Answer Key

- **Q1:** B - Dimethyl glyoxime forms a red precipitate with Ni(II) for detection.
- **Q2:** A - Gold is extracted as the cyanide complex $[\text{Au}(\text{CN})_2]^-$.
- **Q3:** B - Cis-platin $[\text{PtCl}_2(\text{NH}_3)_2]$ is used in cancer treatment.

Memory Aids

- DMG detects Ni by red precipitate formation.

- EDTA titration differentiates Ca^{2+} and Mg^{2+} by stability constants.
- $\text{Ni}(\text{CO})_4$ formation purifies nickel.
- Ziegler-Natta catalyst polymerizes alkenes at room temperature.
- Cis-platin is a platinum coordination compound used in chemotherapy.

Prepzy